

device using the multilayered polymeric film as a separator are also provided. The multilayered polymeric film comprises: (i) a porous first polymer layer; and (ii) a gelled second polymer layer of polyvinylidene fluoride-chlorotrifluoroethylene copolymer. The method comprises the steps of: (i) dissolving polyvinylidene fluoride-chlorotrifluoroethylene copolymer in solvent selected from the group consisting of acetone, dimethylacetamide and N-methyl-2-pyrrolidone; and (ii) after coating or impregnating or simultaneously coating and impregnating one side or both sides of a porous polymer film with the solution of the step (i), drying it to form a gelled second polymer layer. The polymer electrolyte system for an electrochem. device comprises: (i) a multilayered polymeric separator comprising a porous first polymeric layer and a gelled second polymer layer of polyvinylidene fluoride-chlorotrifluoroethylene copolymer; and (ii) a liquid electrolyte comprising a salt and an organic solvent.

IC ICM B32B027-28

CC 38-3 (Plastics Fabrication and Uses)

Section cross-reference(s): 72, 76

L25 ANSWER 8 OF 17 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:414438 HCAPLUS Full-text

DOCUMENT NUMBER: 138:404361

TITLE: Secondary nonaqueous electrolyte battery and its manufacture

INVENTOR(S): Segawa, Masazumi

PATENT ASSIGNEE(S): Japan Storage Battery Co., Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 11 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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JP 2003157898	A	20030530	JP 2001-355042	20011120

PRIORITY APPLN. INFO.:

JP 2001-355042

20011120

AB The battery has an anode and/or a cathode containing a 1st porous polymer electrolyte, and a 2nd porous polymer electrolyte layer (a) between the 2 electrodes or (b) on both sides of a separator; and is obtained by adhering (a) the electrode-electrolyte or (b) the cathode-electrolyte, separator-electrolyte and anode-electrolyte with heat treatment; where the battery satisfies $(T2-4) \leq T1 \leq (T2+5)$ and $T3 \geq (T2+10)$, [$T1$ = heat treatment temperature; $T2$ = initial m.p. of the polymer electrolyte layer observed by DSC; and $T3$ = reaction peak temperature].

IC ICM H01M010-40

ICS H01M004-02

CC 52-2 (Electrochemical, Radiational, and Thermal Energy Technology)

ST porous polymer electrolyte secondary battery manuf; heat treatment DSC specification

IT Secondary batteries

(lithium; manufacture of electrodes containing porous polymer electrolytes for secondary lithium batteries)

IT Battery electrolytes

(manufacture of electrodes containing porous polymer electrolytes for secondary lithium batteries)

IT Fluoropolymers, uses

RL: DEV (Device component use); USES (Uses)
 (manufacture of electrodes containing porous polymer electrolytes for
secondary lithium batteries)

IT 7440-50-8, Copper, uses
 RL: DEV (Device component use); USES (Uses)
 (anode collector; manufacture of electrodes containing porous polymer
 electrolytes for **secondary** lithium batteries)

IT 7782-42-5, Graphite, uses
 RL: DEV (Device component use); USES (Uses)
 (anode; manufacture of electrodes containing porous polymer electrolytes
 for **secondary** lithium batteries)

IT 7429-90-5, Aluminum, uses
 RL: DEV (Device component use); USES (Uses)
 (cathode collector; manufacture of electrodes containing porous polymer
 electrolytes for **secondary** lithium batteries)

IT 143623-51-2, Cobalt lithium nickel oxide (Co_{0.15}LiNi_{0.85}O₂)
 RL: DEV (Device component use); USES (Uses)
 (cathode; manufacture of electrodes containing porous polymer electrolytes
 for **secondary** lithium batteries)

IT 96-49-1, Ethylene carbonate 105-58-8, Diethyl carbonate
 RL: DEV (Device component use); USES (Uses)
 (electrolyte solution; manufacture of electrodes containing porous polymer
 electrolytes for **secondary** lithium batteries)

IT 21324-40-3, Lithium hexafluorophosphate
 RL: DEV (Device component use); USES (Uses)
 (electrolyte; manufacture of electrodes containing porous polymer
 electrolytes for **secondary** lithium batteries)

IT 9011-17-0, Hexafluoropropylene-vinylidene fluoride copolymer
 24937-79-9, PVDF
 RL: DEV (Device component use); USES (Uses)
 (manufacture of electrodes containing porous polymer electrolytes
 for **secondary** lithium batteries)

L25 ANSWER 9 OF 17 HCAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:71260 HCAPLUS Full-text

DOCUMENT NUMBER: 138:138410

TITLE: Porous polyolefinic films containing particles
 and production method thereof

INVENTOR(S): Kishii, Yutaka; Kii, Keisuke; Uetani, Yoshihiro;
 Fujita, Shigeru; Yamaguchi, Mutsuko

PATENT ASSIGNEE(S): Nitto Denko Corp., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 9 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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JP 2003026847	A	20030129	JP 2001-214619	200107 16
PRIORITY APPLN. INFO.:			JP 2001-214619	200107 16

AB Title films useful for separators for nonaq. electrolyte batteries comprise
 polyolefin resins with weight average mol. weight $\geq 5 + 105$ and particles with

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery equipped with the porous polymer electrolyte, and its manufacture approach.

[0002]

[Description of the Prior Art] The nonaqueous electrolyte rechargeable battery by which current marketing is carried out consists of the organic electrolytic solutions which dissolved lithium salt, such as a negative-electrode plate which applied carbon system matter which applied transition-metals multiple oxides, such as a cobalt acid lithium, etc. as an active material, such as a positive-electrode plate and graphite, as an active material, a separator made from polyolefine, and LiPF₆, in carbonate mixed solvents, such as ethylene carbonate. In order to improve the safety of this cell, the attempt which uses a scarce solid-state polymer electrolyte for chemical reactivity instead of the inflammable organic electrolytic solution has been made.

[0003] Recently, in order to raise the ion conductivity of a solid-state polymer electrolyte, to use humidity or the solid-state polymer electrolyte made to swell is tried in the polymer with the organic electrolytic solution. Furthermore, manufacturing the nonaqueous electrolyte rechargeable battery excellent in high charge/discharge capability ability and safety is proposed using a porous polymer electrolyte instead of a separator, and by including a solid-state polymer electrolyte polymer electrolyte all over the hole of an electrode plate as it is indicated by JP,8-195220,A and JP,9-259923,A in order to raise the diffusion rate of a lithium ion for example.

[0004] A porous polymer electrolyte has the conductivity and the diffusion coefficient of a lithium ion higher than the conventional polymer electrolyte of non-porosity. If an electrode is equipped with a porous polymer electrolyte, since maldistribution-ization of the electrolytic solution accompanying the repeat of a charge-and-discharge reaction will be controlled, it becomes possible to control lowering of the discharge capacity accompanying a cycle. This is because the porous polymer electrolyte with which the electrode plate was equipped holds the electrolytic solution inside an electrode. Moreover, this porous polymer electrolyte is because omission of active material particles can be controlled in order to achieve the function as a binder.

[0005] Moreover, if both sides of a separator are equipped with this porous polymer electrolyte again at the part of a separator, when the amount of electrolytic solutions held in a cell is reduced, lowering of high charge/discharge capability ability will be controlled. Furthermore, since swelling or the porous polymer electrolyte which carried out humidity is soft, it combines with the irregularity of forward and a negative electrode, and a configuration changes with the electrolytic solutions. Therefore, it is possible to narrow the gap of a porous polymer electrolyte and an electrode plate.

[0006] Moreover, in order to raise the high-rate-discharge property of a nonaqueous electrolyte rechargeable battery, one [at least] electrode plate of a positive-electrode plate and a negative-electrode plate is equipped with a porous polymer electrolyte, it has a porous polymer electrolyte layer between a positive-electrode plate and a negative-electrode plate, and fixing a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate is examined.

[0007] Furthermore, one [at least] electrode and both sides of a separator are equipped with a porous polymer electrolyte layer, and fixing a positive-electrode plate, a porous polymer electrolyte layer and a porous polymer electrolyte layer, a separator and a negative-electrode plate, and a porous polymer electrolyte layer is examined.

[0008] Since the increment in the cell thickness accompanying a cycle is controlled in these cases, the cycle engine performance can be improved by leaps and bounds than the case where only the interior of an electrode is equipped with a porous polymer electrolyte.

[0009]

[Problem(s) to be Solved by the Invention] However, when a porous polymer electrolyte is used as a separator, also in any in the case of having arranged to both sides of a separator, there is still a clearance between the boundary section of a porous polymer electrolyte and an electrode and a porous polymer electrolyte, and a separator. Diffusion of ion is checked in this part. Therefore, when high rate discharge was performed, the new problem that discharge capacity fell remarkably arose. This inclination becomes remarkable especially, when there are few amounts of electrolytic solutions.

[0010] Moreover, when fixing processing is performed, a cell may not show sufficient high-rate-discharge engine performance. heat-treatment of a cell -- if a porous polymer electrolyte layer dissolves remarkably, the micropore blockades. Consequently, it is thought that it is because the ionic conductivity in the polymer electrolyte layer and the diffusion rate of the lithium ion in charge-and-discharge reaction time fell. The degradation becomes remarkable especially, when the amount of electrolytic solutions is reduced, in order to improve the safety of a cell.

[0011] This invention is made in order to solve this problem, and it aims at offering the nonaqueous electrolyte rechargeable battery which raised the high-rate-discharge engine performance at the time of reducing the high-rate-discharge engine performance, especially the amount of electrolytic solutions, and its manufacture approach.

[0012]

[Means for Solving the Problem] Invention of claim 1 equips either [at least] a positive-electrode plate or a negative-electrode plate with a porous polymer electrolyte. In the manufacture approach of the nonaqueous electrolyte rechargeable battery which was equipped with the porous polymer electrolyte layer between the positive-electrode plate and the negative-electrode plate, and the positive-electrode plate, the porous polymer electrolyte layer, and the negative-electrode plate fixed by heat-treatment The fusion initiation temperature of the porous polymer electrolyte layer observed by T1 (degree-C) differential scan heat measurement in the heat-treatment temperature of said nonaqueous electrolyte rechargeable battery T2 (degree C), When reaction peak temperature is made into T3 (degree C), it is characterized by filling the relation between $T2-4 \leq T1 \leq T2+5$ and $T3 \geq T2+10$.

[0013] According to invention of claim 1, where lock out of the micropore of the porous polymer electrolyte layer accompanying heat-treatment is controlled, since a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate can be fixed, the capacity lowering at the time of high rate discharge is controlled.

[0014] Invention of claim 2 equips either [at least] a positive-electrode plate or a negative-electrode plate with a porous polymer electrolyte. Both sides of a separator are equipped with a porous polymer electrolyte layer. A positive-electrode plate and a porous polymer electrolyte layer, In the manufacture approach of the nonaqueous electrolyte rechargeable battery which the separator, the porous polymer electrolyte layer, and a negative-electrode plate and a porous polymer electrolyte layer fixed by heat-treatment The fusion initiation temperature of the porous polymer electrolyte layer observed by T1 (degree-C) differential scan heat measurement in the heat-treatment temperature of said nonaqueous electrolyte rechargeable battery T2 (degree C), When reaction peak temperature is made into T3 (degree C), it is characterized by filling the relation between $T2-4 \leq T1 \leq T2+5$ and $T3 \geq T2+10$.

[0015] According to invention of claim 2, where lock out of the micropore of the porous polymer electrolyte layer accompanying heat-treatment is controlled, since a positive-electrode plate, a porous polymer electrolyte layer and a negative-electrode plate, a porous polymer electrolyte layer, and a separator and a porous polymer electrolyte layer can be fixed, the capacity lowering at the time of high rate discharge is controlled.

[0016] In the nonaqueous electrolyte rechargeable battery by which invention of claim 3 was produced by the manufacture approach according to claim 1 or 2, the gas in a cell is characterized by the volume of the electrolytic solution being 100% or less 30% or more to the total hole volume of a positive-electrode plate, a negative-electrode plate, a porous polymer electrolyte layer, and a separator including the carbon dioxide more than 1 volume %.

[0017] According to invention of claim 3, lowering of the high-rate-discharge capacity of the cell at the time of reducing the amount of electrolytic solutions is controlled.

[0018]

[Embodiment of the Invention] In the manufacture approach of the nonaqueous electrolyte rechargeable battery (it only considers as a cell hereafter) of this invention, when a positive-electrode plate, a porous polymer electrolyte layer and a negative-electrode plate, a porous polymer electrolyte layer, and a separator and a porous polymer electrolyte layer dissolve ["it has fixed" and] a part of the polymer electrolyte layer by heat-treatment, it means that the electrode plate, the porous polymer electrolyte layer, and a separator and a porous polymer electrolyte layer are unified (junction). It is difficult to disassemble a cell, and to dissociate, without destroying these elements by the usual approach, even when it is small.

[0019] In this invention, in order to fix a porous polymer electrolyte layer and other cell elements, a cell is heat-treated.

By heat-treatment, a part of porous polymer electrolyte layer dissolves. It will be in the condition that the electrode plate and the porous polymer electrolyte layer joined on that occasion, and in the cooling process of a subsequent cell, the polymer electrolyte layer in the condition of having dissolved is solidified, and it is thought that an electrode plate and a polymer electrolyte layer fix. This is considered to pass through the same process also about fixing with a porous polymer electrolyte layer and a separator.

[0020] In this invention, when T_2 (degree C) and reaction peak temperature are made into T_3 (degree C) for the fusion initiation temperature of the porous polymer electrolyte layer observed by T_1 (degree-C) differential scan heat measurement in the heat-treatment temperature of a cell, it is characterized by filling the relation between $T_2-4 \leq T_1 \leq T_2+5$ and $T_3 \geq T_2+10$. In this case, where lock out of the hole of a porous polymer electrolyte layer is controlled, that polymer electrolyte layer and electrode plate, or its polymer electrolyte layer and separator can be fixed. Consequently, in order for the diffusibility ability of a lithium ion not to fall, the high-rate-discharge performance degradation of a cell can be controlled.

[0021] If heat-treatment temperature is carried out to beyond the peak temperature of the fusion reaction of the polymer electrolyte layer observed by differential scan heat (DSC) measurement when fixing an electrode plate, a porous polymer electrolyte layer, or a separator and a porous polymer electrolyte layer by heat-treatment, fusion of a polymer electrolyte layer is promoted remarkably and the hole of a polymer electrolyte layer blockades remarkably between short time extremely.

[0022] Then, it turned out that the fusion reaction rate of a porous polymer electrolyte layer falls, and rapid lock out of the hole is remarkably controlled by the conditions of $T_2-4 \leq T_1 \leq T_2+5$ by heat-treating. However, it is necessary to fulfill the conditions of $T_3 \geq T_2+10$ simultaneously. When the heat-treatment temperature T_1 becomes close to peak temperature T_3 of the fusion reaction of a porous polymer electrolyte layer, the melting rate of a porous polymer electrolyte layer is because it becomes remarkably high.

[0023] In order to make high-fixing reinforcement of an electrode plate and a porous polymer electrolyte layer, and fixing reinforcement of a separator and a polymer electrolyte layer, it is good to adjust heating time. The time amount is good to determine in consideration of the class of cell case, the magnitude of a cell, the melting point of the polymer electrolyte layer which it had between the positive-electrode plate and the negative-electrode plate, etc.

[0024] The fusion initiation temperature of a porous polymer electrolyte layer is the initiation temperature of the endothermic reaction accompanying the fusion which performs differential scan heat (DSC) measurement in the condition of having filled the hole of a porous polymer layer with the electrolytic solution, and is observed in the measurement. Moreover, temperature which shows the maximum point of the endothermic reaction observed in DSC measurement is made into the peak temperature of a reaction. In addition, when broadcloth [the peak of the endothermic reaction accompanying a fusion reaction], initiation of endothermic reaction and the mean value of termination temperature are made into peak temperature.

[0025] As for the nonaqueous electrolyte rechargeable battery of this invention, the gas in a cell is further characterized by the volume of the electrolytic solution being 100% or less 30% or more to the total hole volume of a positive-electrode plate, a negative-electrode plate, a porous polymer electrolyte layer, and a separator including the carbon dioxide more than 1 volume %. In addition, in this invention, "the hole volume of a porous polymer electrolyte layer" means the hole volume in the condition excluding the electrolytic solution from the porous polymer electrolyte layer. Furthermore, as a short circuit inhibitor of a positive-electrode plate and a negative-electrode plate, when only a porous polymer electrolyte layer is used, the hole volume of a separator is zero. In this case, the volume of the electrolytic solution is characterized by being 100% or less 30% or more to the total hole volume of a positive-electrode plate, a negative-electrode plate, and a porous polymer electrolyte layer.

[0026] Here, the content of the carbon dioxide in the gas in a cell is defined by $x(\text{volume [of a carbon dioxide]} / (\text{volume of gas of volume + and others of carbon dioxide})) 100\text{-}/\text{volume } \%$. The volume of those gas can be measured by the gas chromatograph.

[0027] In this invention, the high-rate-discharge engine performance of the cell at the time of reducing the amount of electrolytic solutions is improvable by carrying out content of the carbon dioxide in the gas in a cell to more than 1 volume %. The reason is as follows. In the case where the amount of electrolytic solutions is reduced, even when an electrode is equipped with a porous polymer electrolyte, the part which the electrolytic solution and a negative-electrode active material do not contact certainly exists. In the part, since a solid electrolyte coat is not formed, the diffusion rate of a lithium ion falls extremely. Consequently, the high-rate-discharge engine performance falls.

[0028] However, if a carbon dioxide is enclosed with the interior of a cell, in the negative-electrode active material front face which does not contact the electrolytic solution, a carbon dioxide will be returned and the coat of a lithium carbonate will be formed. Consequently, lowering of the diffusibility ability of a lithium ion is controlled. By the cell

of the former [contain / only the carbon dioxide of about 0.03 volume %], there was such no effectiveness into air. [0029] Moreover, in this invention, the volume of the electrolytic solution may be 100% or less 30% or more to the total hole volume of a positive-electrode plate, a negative-electrode plate, a porous polymer electrolyte layer, and a separator. In such a cell, the effectiveness that the high-rate-discharge performance degradation by enclosing a carbon dioxide with the interior of a cell is controlled becomes remarkable. Furthermore, in order that the inflammable electrolytic solutions may decrease in number substantially, the safety of a cell improves remarkably.

[0030] Here, the total hole volume of a positive-electrode plate, a negative-electrode plate, a porous polymer electrolyte layer, and a separator can be determined as follows. First, a positive-electrode plate, a negative-electrode plate, a porous polymer electrolyte layer, and a separator are taken out from the cell which repeated charge and discharge 5 times or more. This is removed when a separator is not used. Next, solvents, such as dimethyl carbonate (DMC), wash them, and after drying, those hole volume is measured by the mercury porosimeter. Let the sum of those hole volume be the total hole volume.

[0031] In addition, when the amount of electrolytic solutions is reduced, it is desirable to make high content of the carbon dioxide contained in a cell, and it is desirable to carry out to more than 30 volume % especially. The reason is that it can form the coat of a lithium carbonate in the negative-electrode active material front face on which the electrolytic solution does not contact certainly.

[0032] Many holes are formed in the polymer electrolyte which has ion conductivity, the organic electrolytic solution was made to hold in the hole, and, as for the porous polymer electrolyte in this invention, ion conductivity is shown by the amount of [both] polymer part and pore. Furthermore, it is desirable that a porous polymer electrolyte is network structure, and it is desirable that it is especially three-dimensions network structure.

[0033] This invention is characterized by equipping one [at least] electrode plate of a positive-electrode plate and a negative-electrode plate with a porous polymer electrolyte. The electrode plate is equipped with the porous binder layer containing an active material, and the electrode plate equipped with the porous polymer electrolyte means that to which a porous polymer electrolyte exists in the hole and binder layer front face of the binder layer. Although a porous polymer electrolyte is good to exist at least in the part in the hole of the binder layer which constitutes an electrode plate, it is desirable to be distributed in the hole of the plied timber layer at homogeneity. Moreover, although either [at least] the positive-electrode plate or the negative-electrode plate should just be equipped with the porous polymer electrolyte, it is desirable that both electrode plates are equipped with the porous polymer electrolyte.

[0034] If the hole of the plied timber layer of an electrode plate is equipped with a porous polymer electrolyte, in order that the polymer electrolyte may work as a binder, omission from the plate of the active material accompanying the repeat of a charge-and-discharge cycle are controlled. Furthermore, when a porous polymer electrolyte swells with the electrolytic solution, distribution of the electrolytic solution in the active material layer of an electrode becomes homogeneity, and the charge-and-discharge cycle engine performance improves.

[0035] In this invention, "the porous polymer electrolyte layer which it has between a positive-electrode plate and a negative-electrode plate" means that a porous polymer electrolyte layer is used as a separator which prevents the short circuit of a positive-electrode plate and a negative-electrode plate. As for the thickness, it is desirable that it is 5 micrometers or more that what is necessary is just the thickness which can prevent the short circuit of a positive-electrode plate and a negative-electrode plate. Moreover, in order to make the energy density of a cell high, as for the thickness, it is desirable that it is 40 micrometers or less.

[0036] When the film which has the micropore made from polyolefine is used as a separator, it means arranging a porous polymer electrolyte layer between the separator and positive-electrode plate and between the separator and negative-electrode plate. With the film which has the micropore made from polyolefine, the thing which produced leading micropore, a porous nonwoven fabric, etc. are raised to insulating film, such as polypropylene and polyethylene. In addition, you may have a porous polymer electrolyte all over the hole of a separator. Since the polymer which constitutes the former insulating film does not contain the electrolytic solution in the matrix, the difference between a separator and a porous polymer electrolyte layer is that ion conductivity is not shown. The sum total thickness of the porous polymer electrolyte layer with which a separator and its both sides were equipped is good to be referred to as 5 micrometers or more 40 micrometers or less.

[0037] One example of the manufacture approach of the cell by this invention is described below. The approach equips one [at least] electrode plate of a positive-electrode plate and a negative-electrode plate with a porous polymer. The process which assembles the cell equipped with the porous polymer layer between the positive-electrode plate and the negative-electrode plate, By pouring the electrolytic solution in the cell, the porous polymer and a porous polymer layer. The process used as a porous polymer electrolyte and a porous polymer electrolyte layer, respectively, the process which encloses a carbon dioxide with the interior of a cell, and the process which fixes a positive-electrode plate, a

porous polymer electrolyte layer, and a negative-electrode plate by heat-treating on a cell are included.

[0038] In this invention, the gas in a cell produces the cell containing the carbon dioxide more than 1 volume % by putting in a carbon dioxide in a cell and closing the hole of a container. By this approach, the content of a carbon dioxide can be adjusted easily [an optimum value]. On the other hand, after closing the container of a cell, by the approach of generating a carbon dioxide in it, control of the yield is difficult.

[0039] Here, the process which encloses a carbon dioxide may be carried out before the process which puts in the electrolytic solution, and may be carried out after that. Moreover, a carbon dioxide and the electrolytic solution may be put in simultaneously. Furthermore, the process of first time charge may be carried out before the process which puts in a carbon dioxide, and may be carried out after that.

[0040] Since distribution of the liquid is uneven after putting the electrolytic solution into a cell until it repeats charge and discharge, it is desirable that a carbon dioxide is in a cell at the time of first time charge as for close. If a uniform coat is formed in the front face of a negative-electrode active material of it, since diffusion distribution of a lithium ion will become uniform by it, it is thought that a deposit of a metal lithium can be prevented. Furthermore, the process which closes the container of a cell may be carried out before the process of first time charge, and may be carried out after that.

[0041] Furthermore, after decompressing a cell in this invention, it is desirable to put in a carbon dioxide. By this manufacture approach, since a carbon dioxide can be promptly put in in a cell, productivity improves. It is desirable then to decompress a cell to 0.09 or less MPas. Furthermore, it is desirable to set the pressure to 0.05 or less MPas and 0.01 more MPas or less. Moreover, it is desirable that the pressure inside the cell after closing the hole of the container of a cell is below a pressure of the cell exterior.

[0042] Heat-treatment of a cell is performed after the process which pours in the electrolytic solution. Especially the thing performed after the electrolytic solution is distributed over the hole of a cell component at homogeneity is desirable. The reason is that the polymer electrolyte layer and an electrode plate do not fix to homogeneity that electrolytic-solution distribution of the porous polymer electrolyte layer which it had between the positive-electrode plate and the negative-electrode plate is uneven. Then, heat-treatment is good to carry out, after performing preliminary charge. In addition, when a polymer shows ion conductivity independently, you may heat-treat, before pouring in the electrolytic solution.

[0043] Moreover, heat-treatment of a cell may be performed to any before and behind the process which encloses a carbon dioxide with the interior of a cell. Furthermore, obturation of a cell case may be performed to any before and behind heating down stream processing.

[0044] When bulging of the cell case accompanying volatilization of the electrolytic solution by heat-treatment of a cell arises, it is good to exchange a cell case. Moreover, it is good by opening the obturation section once to emit the gas inside a case and to obturate again. When enclosing a carbon dioxide, the process may be performed before the 2nd obturation.

[0045] There is immersion to a water bath, an oil bath, etc. which heat-pressed [arrangement into the thermostat of a cell and / of the cell], and were heated as a means to heat a cell etc. Also in these, especially the immersion to a water bath, an oil bath, etc., i.e., heating which used the solvent object, is desirable. The reason is that it can heat the whole cell even to the target temperature at homogeneity. When using a thermostat, T1 uses the actual measurement of the temperature inside the tub, and a heat press and it uses the laying temperature and a solvent object, it costs whenever [stoving temperature] for the temperature of the solvent object.

[0046] In this invention, the approach of producing a porous polymer has the breakthrough formation approach, a phase transition method, etc. by UV irradiation. Also in it, the wet method which is one of the phase transition methods is desirable. With the wet method, the produced porous polymer shows a three-dimensional network with many holes.

[0047] When becoming the configuration by which, as for the part, the yarn-like polymer was spread around in the hole when a porous polymer was formed in the hole of the active material layer of an electrode plate, the formation conditions of the location and hole which are formed may show various gestalten. Moreover, a polymer may be humidity or the thing which swells and comes to have ion conductivity by, as for a porous polymer electrolyte, the polymer's itself having ion conductivity, and being immersed in the electrolytic solution.

[0048] A wet method is an approach of obtaining a porous polymer using the 1st solvent in which a polymer is dissolved, and the 2nd solvent for an extract which extracts the 1st solvent from a polymer solution. By immersing the polymer solution which dissolved the polymer into the 2nd solvent which is insoluble to a polymer and has the 1st solvent and compatibility, the 1st solvent of a polymer solution is extracted, the part from which the 1st solvent was removed serves as a hole, and a porous polymer is formed.

[0049] As a polymer used for a porous polymer electrolyte Humidity or the polymer which swells and comes to have

ion conductivity is desirable by the electrolytic solution. For example, poly vinylidene fluoride (PVdF), a polyvinyl chloride, Polyethers, such as a polyacrylonitrile, polyethylene oxide, and polypropylene oxide, A polyvinylidene chloride, polymethylmethacrylate, polymethyl acrylate, It is independent, or polyvinyl alcohol, the poly methacrylonitrile, polyvinyl acetate, a polyvinyl pyrrolidone, polyethyleneimine, polybutadiene, polystyrene, polyisoprenes, or these ***** can be mixed and used. Moreover, the polymer to which copolymerization of the various monomers which constitute the above-mentioned polymer was carried out, for example, vinylidene fluoride / hexafluoropropylene copolymer etc., (P(VdF/HFP)) can also be used. In addition, what has the possible flexibility of configuration change which followed in footsteps of cubical-expansion contraction of the active material by charge and discharge is desirable.

[0050] As the 1st solvent which dissolves a polymer, the ether, such as carbonates, such as dimethylformamide, propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate, wood ether, diethylether, ethyl methyl ether, and a tetrahydrofuran, dimethylacetamide, 1-methyl-pyrrolidinone, N-methyl-2-pyrrolidones, and such mixture can be used according to a polymer.

[0051] What has this and compatibility as the 2nd solvent according to the 1st solvent is chosen, for example, water, alcohol, acetones, and these mixed solutions can be used.

[0052] In this invention, as a porous polymer electrolyte layer which it has between a positive-electrode plate and a negative-electrode plate, you produce what became independent of an electrode plate beforehand, and may also insert between a positive-electrode plate and a negative-electrode plate at the time of a cell assembly. Moreover, a porous polymer electrolyte layer may be directly formed in an electrode plate front face. A porous polymer layer may be directly formed in both sides of separators, such as a product made from polyolefine, further again.

[0053] Moreover, the construction material of the porous polymer electrolyte with which the porous polymer electrolyte layer and electrode plate which it has between a positive-electrode plate and a negative-electrode plate are equipped does not necessarily need to be the same. Furthermore, the construction material of the porous polymer electrolyte with which both sides of a separator are equipped does not need to be the same respectively.

[0054] The multiple oxide which can use the compound which can emit [occlusion and] a lithium as positive active material of the nonaqueous electrolyte rechargeable battery of this invention, for example, is expressed with the empirical formulas Li_xMO_2 , such as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , or $\text{Li}_y\text{M}_2\text{O}_2$ (however, M transition metals, $0 < x \leq 1$, $0 < y \leq 2$), the oxide which has a tunnel-like hole, the metal chalcogen ghost of the layer structure, etc. can be used. Moreover, the inorganic compound which permuted some transition metals M by at least one or more kinds of other elements can also be used like $\text{LiNi}_{0.80}\text{Co}_{0.20}\text{O}_2$ grade. Furthermore, organic compounds, such as the poly aniline, can also be used, for example. In addition, the various above-mentioned active materials can also be mixed and used.

[0055] As a negative-electrode active material of the nonaqueous electrolyte rechargeable battery of this invention, carbon materials, such as transition-metals oxide, such as transition-metals multiple oxides, such as a lithium alloy with Li, aluminum, Si, etc. and LiFe_2O_3 , and WO_2 , MoO_2 , hard carbon, and a graphite, lithium nitride, metal lithiums, or such mixture can be used, for example. as a carbon material -- graphite ingredients, such as nongraphitizing carbon, such as graphitizing carbon, such as corks, a meso carbon micro bead (MCMB), a mesophase pitch based carbon fiber, and a pyrolysis vapor growth carbon fiber, a phenol resin baking object, a polyacrylonitrile system carbon fiber, a pseudo-isotropic carbon, and a furfuryl-alcohol-resin baking object, a natural graphite, an artificial graphite, Graphitization MCMB, a graphitization mesophase pitch based carbon fiber, and a graphite whisker, -- such mixture exists further. If these carbon system ingredients are used as an active material, the effectiveness at the time of enclosing a carbon dioxide with the interior of a cell will become remarkable.

[0056] As an electrolytic-solution solvent of the nonaqueous electrolyte rechargeable battery of this invention, polar solvents, such as ethylene carbonate, dimethyl carbonate, 1, and 2-dimethoxyethane, or such mixture can be used. Moreover, as a salt which the electrolytic solution is made to contain, the lithium salt of LiPF_6 and LiBF_4 grade or such mixture can be used.

[0057] The amount of pouring in of the electrolytic solution is good to consider as 140% or less of the hole volume (for the amount of porous polymer electrolyte to remove) sum total of a positive electrode, a negative electrode, a porous polymer electrolyte layer, and a separator, and 30% or more, and good to consider as the amount which can follow in footsteps of expansion contraction of the electrode volume according to electrode construction material at worst. If it carries out 100% or less to 30% or more of the total hole volume of the above-mentioned cell element when enclosing a carbon dioxide with the interior of a cell, the effectiveness of this invention will become remarkable.

[0058]

[Example] Hereafter, an example explains this invention further. In the nonaqueous electrolyte rechargeable battery of

an example and the example of a comparison, all of a positive-electrode plate, a negative-electrode plate, the electrolytic solution, and a cell configuration used the same thing shown below.

[0059] First, PVdF3.6wt%, the paste which mixed NMP40wt% was applied to both sides of aluminium foil, it dried at 90 degrees C, NMP was evaporated, and the body of a positive electrode was prepared acetylene black 2.4wt% LiNi0.85Co0.15O2 particle 54.0wt%.

[0060] next, P (VdF/HFP) (weight average molecular weight about 2.50×10^5) which copolymerized 5wt% HFP -- NMP -- 8wt(s)% -- the polymer solution in which it was made to dissolve was prepared. The above-mentioned body of a positive electrode was immersed into the polymer solution, and the polymer solution was sunk in all over the hole of the body of a positive electrode. And after removing through the polymer solution which adhered to the surplus in the electrode surface on a roller, the body of a positive electrode was immersed in ion exchange water (25 degrees C), and NMP was extracted.

[0061] It dried at ejection and 130 degrees C, and this electrode was pressed after that. The thickness of the positive-electrode plate after a press was 160 micrometers. The mass of the active material with which per positive-electrode plate unit area was filled up was 19 mg/cm². Let this be the positive-electrode plate P1.

[0062] in addition, the mixture of the electrode with which the voidage of an electrode is calculated from each consistency of an active material, a binder, and a conductive assistant -- it calculates from a consistency, the appearance volume calculated from the appearance (length, width, thickness) dimension of an electrode, and the weight of an electrode. The same is said of the following.

[0063] Next, graphite was used as a negative-electrode active material, and the negative electrode was produced as follows. Graphite 81wt%, PVdF9wt%, the paste which mixed NMP10wt% was applied to both sides of copper foil with a thickness of 14 micrometers, it dried at 90 degrees C, NMP was evaporated, and the body of a negative electrode was prepared.

[0064] next, P (VdF/HFP) (weight average molecular weight about 2.50×10^5) which copolymerized 5wt% HFP -- NMP -- 6wt(s)% -- the polymer solution in which it was made to dissolve was prepared. The above-mentioned body of a negative electrode was immersed into the polymer solution, and the polymer solution was supported all over the hole of the body of a negative electrode. And after removing through the polymer solution which adhered to the surplus in the electrode surface on a roller, the body of a negative electrode was immersed in ion exchange water (25 degrees C), and NMP was extracted.

[0065] It dried at ejection and 100 degrees C, and this electrode was pressed after that. The thickness of the negative-electrode plate after a press was 208 micrometers. The mass of the active material with which per negative-electrode plate unit area was filled up was 14 mg/cm². Let this be the negative-electrode plate N1. In addition, after the porous polymer with which the interior of the electrode of the positive-electrode plate P1 and the negative-electrode plate N1 was equipped pours the electrolytic solution in a cell, it absorbs or swells the electrolytic solution and serves as a porous polymer electrolyte.

[0066] Thus, combining the positive-electrode plate P1 and the negative-electrode plate N1 which were produced, and various porous polymer electrolyte layers, it wound, and considered as the winding mold group of electrode, this was inserted in the case made from aluminum, and the cell was assembled. Then, the mixed electrolytic solution (volume ratio 3:7) of ethylene carbonate and diethyl carbonate which dissolved LiPF6 of 1 mol/l was added and obturated. The amount of pouring in of the electrolytic solution was made into the amount with which 120% of the hole volume sum total of a positive-electrode plate, a negative-electrode plate, and a porous polymer electrolyte layer is filled. In addition, the hole volume of the porous polymer electrolyte layer in this example means the thing of the hole volume at the time of removing the electrolytic solution, i.e., the hole volume of a porous polymer layer. Then, preliminary charge was promptly carried out with the 120mA current for 1 hour, and the nonaqueous electrolyte cell of design-capacity 600mAh was produced.

[0067] The porous polymer layer which it has between a positive-electrode plate and a negative-electrode plate was produced as follows. Poly vinylidene fluoride (PVdF) (weight average molecular weight about 2.43×10^5) was used as construction material of a porous polymer electrolyte. The polymer solution which consists of PVdF20wt% and NMP80wt% was prepared. this polymer solution -- a glass plate top -- a doctor blade method -- using -- the cast -- carrying out -- ethanol -- 75wt(s)% -- it was immersed into the included ion exchange water, and the porous polymer layer was produced. The thickness was 25 micrometers and voidage was 70%. This is set to SP1. In addition, in the condition of having included the electrolytic solution (mixed electrolytic solution of ethylene carbonate and diethyl carbonate which dissolved one mol [l.] LiPF6 (volume ratio 3:7)), the result which carried out differential-scanning-calorimetry (DSC) measurement is shown to porous polymer layer SP1 at drawing 1. From drawing 1, the peak temperature of 100 degrees C and the fusion reaction of those was judged to be 114 degrees C for the fusion initiation

temperature of SP1 electrolyte layer.

[0068] moreover, instead of [of PVdF which is the construction material of the above SP 1] -- HFP -- 5wt(s)% -- porous polymer layer SP2 using the copolymerized poly vinylidene fluoride (P(VdF/HFP)) (weight average molecular weight about 2.73×10^5) as construction material was produced. The thickness was 25 micrometers and voidage was 70%. When DSC measurement was given to SP2 for the above-mentioned electrolytic solution in ** and a condition, the peak temperature of 100 degrees C and the fusion reaction of those of the fusion initiation temperature was 110 degrees C.

[0069] moreover, instead of [of PVdF which is the construction material of the above SP 1] -- HFP -- 11wt(s)% -- porous polymer layer SP3 using the copolymerized poly vinylidene fluoride (P(VdF/HFP)) (weight average molecular weight about 2.56×10^5) as construction material was produced. The result of having given SP3 DSC measurement in the condition of having included the above-mentioned electrolytic solution is shown in drawing 2 . From drawing 2 , the peak temperature of 94 degrees C and the fusion reaction of those of the fusion initiation temperature of SP3 electrolyte layer was 103 degrees C.

[0070] These porous polymer layers were used and nine kinds of cells of cell A-I were produced using the positive-electrode plate P1 and the negative-electrode plate N1, and where these cells are inserted into a griddle, it heat-treated. In addition, a porous polymer layer turns into a porous polymer electrolyte layer by including the electrolytic solution. Heating of a cell was performed using the oil bath. Here, the heat-treatment temperature investigated ***** effect to fixing with a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate and a porous polymer electrolyte layer. The cell after heat-treatment was disassembled and the existence [layer / these electrode plates and / porous / polymer electrolyte] of fixing was investigated. Moreover, the structural change of the micropore of the cross section of the porous polymer electrolyte layer accompanying heat-treatment was investigated by SEM observation. Those results are shown in a table 1. In the assessment column of the positive-electrode plate of a table 1, a porous polymer electrolyte layer, a negative-electrode plate, and fixing, it means that O fixed and means that x had not fixed.

[0071]

[A table 1]

電池	多孔性 ポリマ ー層	加熱処 理 温 度℃	加熱時間 h r	正極板と多孔性ポリ マー電解質層と負極 板との固着の有無	加熱処理に伴う微細 孔の形状変化
A	SP1	93	3	×	変化なし
B	SP1	96	1	○	ほとんど閉塞なし
C	SP1	100	0.45	○	ほとんど閉塞なし
D	SP1	105	0.4	○	ほとんど閉塞なし
E	SP1	107	0.2	○	一部閉塞
F	SP2	96	1	○	ほとんど閉塞なし
G	SP2	105	0.4	○	ほとんど閉塞なし
H	SP3	90	1	○	半数が閉塞
I	SP3	99	0.2	○	ほとんどが閉塞

[0072] The result of Cell A showed that a positive-electrode plate, and its polymer electrolyte layer SP 1 and negative-electrode plate could not be fixed, when whenever [stoving temperature] was made lower 7 degrees C than the fusion initiation temperature of a porous polymer electrolyte layer.

[0073] When whenever [stoving temperature] is made lower 4 degrees C than the fusion initiation temperature, fixing with a positive-electrode plate, its polymer electrolyte layer, and a negative-electrode plate and its polymer electrolyte layer is possible, and the result of Cells B and F showed that lock out of the micropore of the polymer electrolyte layer was moreover hardly checked.

[0074] When whenever [stoving temperature] was made higher 5 degrees C than the fusion initiation temperature of a porous polymer electrolyte layer, the result of Cells D and G showed that a positive-electrode plate, a porous polymer

electrolyte layer, and a negative-electrode plate could be fixed in the condition that the micropore of the polymer electrolyte layer is hardly blockaded.

[0075] Moreover, when whenever [stoving temperature] was made higher [7 degrees C] from the result of Cell E than the fusion initiation temperature of a porous polymer electrolyte layer, although fixing with a positive-electrode plate, its polymer electrolyte layer, and a negative-electrode plate was possible, it turned out that a part of micropore of the electrolyte layer blockades.

[0076] These results showed that heating conditions needed to fill the relation of $T2-4 \leq T1 \leq T2+5$, when fusion initiation temperature of a $T1$ (degree-C) porosity polymer electrolyte layer was set to $T2$ (degree C) for heat-treatment temperature.

[0077] However, in Cells H and I, in spite of having performed heating at the temperature made lower 4 degrees C than the fusion initiation temperature of a porous polymer, or temperature high 5 degrees C, lock out of the micropore was checked. In the polymer electrolyte SP 3, the difference of the fusion initiation temperature and peak temperature is narrow.

[0078] For this reason, it is thought that the fusion reaction rate of that electrolyte layer was very high when it heat-treated, and most micropores blockaded according to the conditions of $T2-4 \leq T1 \leq T2+5$. Therefore, when fusion peak temperature of a porous polymer electrolyte layer was made into $T3$, it turned out that it is necessary to use the construction material with which the conditions of $T3 \geq T2+10$ are filled.

[0079] Next, Cells A, B, C, D, E, and H were used, and the high-rate-discharge engine performance of a cell was evaluated. At the room temperature, to 4.2V, it charged, and continuously, charge of a cell is the constant voltage of 4.2V, and was performed according to 120mA constant current for a total of 5 hours. The room temperature performed discharge to 2.75V by constant current (120mA and 1200mA), and the discharge capacity at that time was calculated. These results were summarized in a table 2.

[0080]
[A table 2]

電 池	1 2 0 m A 放 電 容 量 m A h	1 2 0 0 m A 放 電 容 量 m A h
A	5 9 8 ~ 6 0 5	3 2 0 ~ 3 3 1
B	6 0 2 ~ 6 0 8	4 7 9 ~ 4 8 9
C	6 0 1 ~ 6 0 4	4 7 4 ~ 4 8 5
D	5 9 9 ~ 6 0 5	4 7 2 ~ 4 8 1
E	5 9 9 ~ 6 0 2	3 7 8 ~ 3 8 2
H	6 0 0 ~ 6 0 4	3 6 7 ~ 3 7 6

[0081] It was almost the same when which cell was used about 120mA discharge capacity. However, by the cell A of the example of a comparison which a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate and its polymer electrolyte layer did not fix, 1200mA discharge capacity is low. On the other hand, when the electrode plate and the porous polymer electrolyte layer fixed, the result of Cells B; C, and D showed that 1200mA discharge capacity became high. Moreover, when a porous polymer electrolyte layer and a negative-electrode plate fixed and the micropore of the polymer electrolyte layer blockaded from Cells E and H, it turned out that there is little augend of 1200mA discharge capacity.

[0082] The carbon dioxide was enclosed with the interior of a cell in order to control the capacity lowering at the time of high rate discharge next, when the amount of electrolytic solutions is reduced. First, the cell was produced combining porous polymer layer SP1, the positive-electrode plate P1, and the negative-electrode plate N1. Next, 20% - 100% of the amount of electrolytic solutions was poured into the cell to the total hole volume. Then, after putting a cell under reduced pressure of 0.008MPa(s) and putting in the carbon dioxide in the cell, the cell of nominal capacity 600mAh was produced by closing the hole of the container of a cell by charging with the current value of 120mA for 1 hour. Then, in order to fix a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate, these cells were heat-treated at 100 degrees C all over the oil bath. The time amount was 0.45 hours. Four kinds of this cell were produced and it considered as Cells J, L, Q, and S.

[0083] Furthermore, as a comparison, although the carbon dioxide was enclosed with the interior of a cell, the cell which does not heat-treat was produced. Four kinds of this cell were produced and it considered as Cells K, M, R, and

T.

[0084] Moreover, when the amount of electrolytic solutions was made into 70%, a carbon dioxide was not enclosed but the cell N which performed only fixing with an electrode plate and a porous polymer electrolyte layer was produced. Furthermore, the cell O which does not perform enclosure and heat-treatment of a carbon dioxide was produced.

[0085] Furthermore, Cell P was produced combining porous polymer layer SP3, the positive-electrode plate P1, and the negative-electrode plate N1. The production approach is as follows. After pouring in the amount of electrolytic solutions 70% to the total hole volume, putting a cell under reduced pressure of 0.008MPa(s) and putting in the carbon dioxide in the cell, the cell of nominal capacity 600mAh was produced by closing the hole of the container of a cell by charging with the current value of 120mA for 1 hour. And in order to fix a positive-electrode plate, a porous polymer layer, and a negative-electrode plate, heat-treatment was performed at 99 degrees C for 0.2 hours.

[0086] The content of cell J-T produced by each to a table 3 was summarized.

[0087]

[A table 3]

電池	電解液量%	多孔性ポリマー層	正・負極板と多孔性ポリマー層との固着の有無	二酸化炭素封入の有無
J	100	SP1	あり	あり
K	100	SP1	なし	あり
L	70	SP1	あり	あり
M	70	SP1	なし	あり
N	70	SP1	あり	なし
O	70	SP1	なし	なし
P	70	SP3	あり	あり
Q	30	SP1	あり	あり
R	30	SP1	なし	あり
S	20	SP1	あり	あり
T	20	SP1	なし	あり

[0088] The high-rate-discharge engine performance was evaluated using these cells. Charge of a cell was continuously charged and charged by the constant voltage of 4.2V to 4.2V according to 120mA constant current at the room temperature for 5 hours. Constant current (120mA and 1200mA) performed discharge to 2.75V at the room temperature. The measurement result of those discharge capacity was summarized in a table 4.

[0089]

[A table 4]

電 池	1 2 0 m A 放 電 容 量 m A h	1 2 0 0 m A 放 電 容 量 m A h
J	5 9 7 ~ 6 0 5	4 7 0 ~ 4 8 1
K	6 0 4 ~ 6 0 8	4 1 5 ~ 4 2 1
L	6 0 3 ~ 6 0 8	4 6 8 ~ 4 7 2
M	6 0 2 ~ 6 0 7	3 8 9 ~ 3 9 9
N	5 9 9 ~ 6 0 2	3 9 0 ~ 4 0 0
O	5 2 0 ~ 5 3 1	1 2 5 ~ 1 3 8
P	6 0 1 ~ 6 0 4	4 0 2 ~ 4 0 7
Q	5 9 9 ~ 6 0 5	4 3 8 ~ 4 4 6
R	5 9 9 ~ 6 0 2	2 8 6 ~ 2 9 9
S	5 7 8 ~ 5 8 4	3 8 0 ~ 3 9 0
T	5 6 5 ~ 5 7 1	2 6 5 ~ 2 7 5

[0090] First, by Cell O, it turned out that both 120mA and 1200mA discharge capacity are low. It turned out that a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate are fixed or that 120mA discharge capacity becomes higher than Cell O by enclosing a carbon dioxide with the interior of a cell.

[0091] Cell N showed that 1200mA discharge capacity increased from Cell O by fixing a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate and its polymer electrolyte layer. This is considered to be because for the clearance between the electrode plates and separators which check diffusion of a lithium ion to have been canceled. However, the capacity is still insufficient.

[0092] Moreover, the result of Cells K, M, and R shows that 1200mA discharge capacity increases from Cell O by enclosing a carbon dioxide with the interior of an electrode. This is considered to be because for the coat of a lithium carbonate to have been formed by having enclosed the carbon dioxide even in the negative-electrode active material particle front face which does not contact the electrolytic solution and directly. However, the capacity is not enough.

[0093] The result of Cells J, L, and Q showed that enclosed a carbon dioxide with the interior of a cell, and the discharge capacity increased remarkably by fixing a positive-electrode plate, a porous polymer electrolyte layer, and a negative-electrode plate further. When SP3 was used as a porous polymer electrolyte layer, Cell P showed that high 1200mA discharge capacity was not obtained.

[0094] When Cells L and P were disassembled and the cross-section structure of a porous polymer electrolyte layer was investigated, in the latter, it turned out to most micropores having not blockaded the former that most micropores blockade.

[0095] In order to control the capacity lowering at the time of the high rate discharge at the time of reducing the amount of electrolytic solutions from this By fixing a positive-electrode plate, its polymer electrolyte layer, and a negative-electrode plate and its polymer electrolyte layer, where lock out of the micropore of a porous polymer electrolyte layer is controlled, and enclosing a carbon dioxide with the interior of a cell It understood that it is necessary to make a solid electrolyte coat form also in the negative-electrode active material particle front face which does not contact the electrolytic solution and directly.

[0096] However, when the amount of electrolytic solutions was made into 20%, it was difficult to control remarkably the capacity lowering at the time of 1200mA discharge only by enclosure of the carbon dioxide inside an electrode, and fixing with an electrode plate and a porous polymer layer.

[0097] The cell equipped with what equipped both sides of the separator made from polypropylene with a thickness of 15 micrometers with various porous polymer electrolyte layers between the positive-electrode plate and the negative-electrode plate next was produced. PVdF used for SP1 was used as construction material of the porous polymer electrolyte layer with which both sides of a separator are equipped. The polymer solution which consists of PVdF20wt% and NMP80wt% was prepared. this polymer solution -- a glass plate top -- a doctor blade method -- using -- the cast -- carrying out -- ethanol -- 75wt(s)% -- it was immersed into the included ion exchange water, and the porous polymer layer was produced. The thickness was 5 micrometers and voidage was 70%. This was made into SP1'.

[0098] as the substitute of PVdF -- HFP -- 5wt(s)% -- porous polymer layer SP2' using the copolymerized poly vinylidene fluoride (P(VdF/HFP)) (weight average molecular weight about 2.73×10^5) as construction material was produced. The thickness was 5 micrometers and voidage was 70%.

[0099] moreover, instead of [of PVdF which is the construction material of above-mentioned SP1'] -- HFP -- 11wt (s)% -- porous polymer layer SP3' using the copolymerized poly vinylidene fluoride (P(VdF/HFP)) (weight average molecular weight about 2.56×10^5) as construction material was produced. The thickness was 5 micrometers and voidage was 70%.

[0100] Between the positive-electrode plate P1 and the negative-electrode plate N1, what equipped both sides of a separator with the porous polymer layer was intervened, and the cell was produced.

[0101] The cell of the same class as above-mentioned cell A-I was produced, and whenever [stoving temperature] investigated ***** effect to fixing with a positive-electrode plate, a porous polymer electrolyte layer and a porous polymer electrolyte layer, a separator and a negative-electrode plate, and a porous polymer electrolyte layer. Moreover, whenever [stoving temperature] investigated ***** effect in the cross-section structure of a porous polymer electrolyte layer. Consequently, the same conclusion as experiment 1 was obtained.

[0102] Next, the cell of the same class as the above-mentioned cells A, B, C, D, E, and H was used, and the high-rate-discharge engine performance was evaluated. At the room temperature, charge of a cell was carried out to 4.2V by 120mA constant current, continuously, is the constant voltage of 4.2V and was performed for a total of 5 hours. The room temperature performed discharge to 2.75V by constant current (120mA and 1200mA), and the discharge capacity at that time was calculated. The discharge engine performance was investigated like the above-mentioned experiment 2. Consequently, the same result as a table 2 was obtained.

[0103] Next the cell of the same class as cell J-T was produced, and fixing with a positive-electrode plate, a porous polymer electrolyte layer and a porous polymer electrolyte layer, a separator and a negative-electrode plate, and a porous polymer electrolyte layer investigated ***** effect for the discharge engine performance at the time of reducing the amount of electrolytic solutions. Moreover, enclosure of the carbon dioxide inside a cell investigated ***** effect for the discharge engine performance at the time of reducing the amount of electrolytic solutions. Consequently, the same result as a table 4 was obtained.

[0104]

[Effect of the Invention] By this invention, where lock out of the micropore of a porous polymer electrolyte layer is controlled, since a positive-electrode plate, the polymer electrolyte layer and a negative-electrode plate, and its polymer electrolyte layer can be fixed, the high-rate-discharge engine performance of a cell improves remarkably.

[0105] Moreover, where lock out of the micropore of a porous polymer electrolyte layer is controlled, since a positive-electrode plate, its polymer electrolyte layer, a separator and its polymer electrolyte layer, and a negative-electrode plate and its polymer electrolyte layer can be fixed, the high-rate-discharge engine performance of a cell improves remarkably.

[0106] Furthermore, in this invention, the gas in a cell becomes effective for control of the capacity lowering at the time of high rate discharge by making the volume of the electrolytic solution into 100% or less 30% or more simultaneously to the total hole volume of a positive-electrode plate, a negative-electrode plate, and a porous polymer electrolyte layer including the carbon dioxide more than 1 volume %.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Either [at least] a positive-electrode plate or a negative-electrode plate is equipped with a porous polymer electrolyte. In the manufacture approach of the nonaqueous electrolyte rechargeable battery which was equipped with the porous polymer electrolyte layer between the positive-electrode plate and the negative-electrode plate, and the positive-electrode plate, the porous polymer electrolyte layer, and the negative-electrode plate fixed by heat-treatment The fusion initiation temperature of the porous polymer electrolyte layer observed by T1 (degree-C) differential scan heat measurement in the heat-treatment temperature of said nonaqueous electrolyte rechargeable battery T2 (degree C), The manufacture approach of the nonaqueous electrolyte rechargeable battery characterized by filling the relation between $T2-4 \leq T1 \leq T2+5$ and $T3 \geq T2+10$ when reaction peak temperature is made into T3 (degree C).

[Claim 2] Either [at least] a positive-electrode plate or a negative-electrode plate is equipped with a porous polymer electrolyte. Both sides of a separator are equipped with a porous polymer electrolyte layer. A positive-electrode plate and a porous polymer electrolyte layer, In the manufacture approach of the nonaqueous electrolyte rechargeable battery which the separator, the porous polymer electrolyte layer, and a negative-electrode plate and a porous polymer electrolyte layer fixed by heat-treatment The fusion initiation temperature of the porous polymer electrolyte layer observed by T1 (degree-C) differential scan heat measurement in the heat-treatment temperature of said nonaqueous electrolyte rechargeable battery T2 (degree C), The manufacture approach of the nonaqueous electrolyte rechargeable battery characterized by filling the relation between $T2-4 \leq T1 \leq T2+5$ and $T3 \geq T2+10$ when reaction peak temperature is made into T3 (degree C).

[Claim 3] The nonaqueous electrolyte rechargeable battery with which the gas in a cell is characterized by the volume of the electrolytic solution being 100% or less 30% or more to the total hole volume of a positive-electrode plate, a negative-electrode plate, a porous polymer electrolyte layer, and a separator including the carbon dioxide more than 1 volume % in the nonaqueous electrolyte rechargeable battery produced by the manufacture approach according to claim 1 or 2.

[Translation done.]